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MEASUREMENT OF RATE CONSTANTS OF ELEMENTARY GAS REACTIONS OF
IMPORTANCE TO UPPER ATMOSPHERE AND COMBUSTION SYSTEMS

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University Professor of Chemistry

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The vibrational energy transfer of highly excited HCl and HF was studied by the infrared chemiluminescence method in a series of five papers. HCl(v < 7) and HF(v < 7) were produced by fast generating reactions, e.g. H + ICl → (v < 7) + I or H + F ₂ → HF(v < 7) + F in large excess He which relaxes the rotational but not the vibrational excitation. With various added quencher gases, about 200 rate constants for stepwise vibrational energy transfer were measured. They tend to increase rapidly with increasing v, often independent of the vibrational energy defect. For HF(v) + HF(0), self-relaxation, the V-V channel decreases from 55% at v=2 to zero at v>5 even though the relaxation rate constant rises as v ^{2.7} . A versatile flow reactor system was built that features three detection methods (laser-induced fluorescence, vacuum u.v. resonance fluorescence, and modulated molecular beam mass spectrometry) plus upstream radical production											
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by IR laser multiphoton decomposition. The $\text{NH}_2 + \text{NO}$ and $\text{CH}_3\text{O} + \text{NO}_2$ reactions were studied successfully. The latter was found to have a recombination (CH_3ONO_2) and disproportionation ($\text{CH}_2\text{O} + \text{HNO}_2$) channel and both were measured indirectly. The $^{18}\text{O} + \text{NO}$ or O_2 isotope exchange reactions were measured, and the results compared with measured and calculated high-pressure limits of the respective recombinations and with NO vibrational relaxation.

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1. Introduction

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The research carried out under this grant falls into three major categories and is described thoroughly in eight publications which are listed in Section 3. It is therefore not necessary to duplicate this detailed description, but highlights of these results will be presented in Section 2. The three categories are: (a) Measurement of vibrational energy transfer rate constants from highly excited HCl and HF to various acceptor molecules; (b) Design and construction of a versatile flow reactor apparatus; and (c) Measurement of important rate processes and comparison with theoretical estimates.

2. Summary of the Most Important Results

In the first of our series of papers on vibrational energy transfer, "Vibrational Relaxation of Highly Excited Diatomics. I. Method, Analysis, and Application to $\text{HCl}(v \leq 7) + \text{CO}_2$ and N_2O ," the infrared chemiluminescence method of I. W. M. Smith and co-workers was adapted to fast flow reactor conditions. A sensitive, liquid N_2 cooled circularly variable filter and InSb detector view the mixing zone in which a "generating" reaction, e.g. $\text{H} + \text{ICl} \rightarrow \text{HCl}(v \leq 7) + \text{I}$ produces infrared chemiluminescence. It is run in great dilution with He such that rotational excitation of $\text{HCl}(v)$ is relaxed but vibrational excitation is not. The chemiluminescent emission spectrum is unfolded, first for the unrelaxed distribution and then for similar, partially relaxed distributions where quencher molecules have been added at known concentrations. A modified Stern-Volmer analysis then calculates specific relaxation rate constants, $k_{v,v-1}^Q$, where Q is the quencher and where it is assumed that energy transfer occurs in single quantum steps, $\Delta v = -1$. This last

assumption has later been relaxed by assuming that 10 or 20% of the vibrational energy transfer proceeded by $\Delta v = -2$ steps, but no substantive change of the rate coefficients was observed. The great advantage of this method is that the fast pumping rate is the reference process of the Stern-Volmer analysis so that the results, even though not highly accurate, are highly consistent with one another.

In the first paper, we reported the energy transfer rate constant of $\text{HCl}(v \leq 7)$ to CO_2 and N_2O which rose from a probability of 5×10^{-3} per Lennard-Jones collision frequency at $v=1$ to 0.40 at $v=7$.

The second paper, "Vibrational Relaxation of Highly Excited Diatomics. II. $\text{HCl}(v \leq 7) + 20$ Quenchers," reported measurements for six diatomic, three triatomic, and eleven polyatomic quenchers. For most of these, k^Q increased with increasing v , independent of whether the vibrational energy gap was reduced or increased. Surprisingly, some large polyatomic molecules, e.g. CF_4 and SF_6 , are very inefficient relaxers whereas hydrocarbons, CH_4 , to iso- C_4H_{10} , are efficient. No single effect, i.e. V-V resonance, dipole interaction, Van der Waals forces, or adduct formation, seems to control the rate of the process. As is seen for both HCl and HF , He and Ar are very inefficient collision partners which leads us to believe that the rotational degrees of freedom in the acceptor molecule are of critical importance.

In the third paper, "Vibrational Relaxation of Highly Excited Diatomics. III. $\text{HF}(v=5,6,7) + \text{H}_2, \text{D}_2, \text{N}_2, \text{HF}, \text{CO}_2, \text{N}_2\text{O}, \text{CH}_4$, and C_2H_6 ," $\text{HF}(v)$ was produced by the highly exothermic $\text{H} + \text{F}_2 \rightarrow \text{HF}(v) + \text{F}$ reaction. The initial, unrelaxed v -distribution was as unrelaxed as Polanyi's low pressure "arrested relaxation" distribution. All quenching rate

constants rose with increasing v , even when the vibrational energy defect increased, as for H_2 and HF. The Lambert-Salter correlation, $\log(v/P)$ vs. ΔE , where P is the relaxation probability per collision, and ΔE is the vibrational energy defect, was reasonable only for $Q = D_2$, because the $HF(v=7 \rightarrow 6)$ quantum is in resonance with $D_2(v=0 \rightarrow 1)$. When expressed in the form of a power law, $k_{v,v-1}^Q \propto v^n$, n ranged from 2 to 8. The highly endothermic relaxation of $HF(v)$ by $HF(v=0)$ is extremely fast, faster than the Lennard-Jones collision frequency for $v=7$, which shows that the process cannot be a $V \rightarrow V$ relaxation.

The fourth paper, "Vibrational Relaxation of Highly Excited Diatomics. IV. $HF(v=1-7) + CO_2$, N_2O , and HF ," extended the v -range of HF by using an additional four generating reactions, viz. $F + HBr \rightarrow HF(v \leq 4) + Br$, $F + CH_4 \rightarrow HF(v \leq 3) + CH_3$, $F + H_2 \rightarrow HF(v \leq 3) + H$, and $F + H_2O \rightarrow HF(v=1) + OH$. All initial v -distributions were compared with published results and found to be in very good agreement. All seven relaxation rate constants were then measured and compared with other published work. The agreement with direct laser excitation studies by Crim and coworkers was excellent. The Lambert-Salter correlations for CO_2 and N_2O look reasonably normal, based on transfer to the asymmetric ν_3 vibration of 2349 or 2224 cm^{-1} , but the relaxation rate constants are too fast for the large energy defects of ~ 600 to 1700 cm^{-1} . For $Q = HF(v=0)$, the Lambert-Salter correlation makes no sense at all, since the energy transfer becomes faster as the energy defect becomes larger. Interestingly power law plots for all three quenchers are reasonably linear and have similar slopes (2.8 for CO_2 , 3.0 for N_2O , and 2.7 for HF). For the HF-HF case, classical and semiclassical trajectory calculations have been published that are in fair agreement with our experimental data for low v , but miss at high v .

In the fifth paper, "Vibrational Relaxation of Highly Excited Diatomics. V. The V-V Channel in $\text{HF}(v) + \text{HF}(0)$ Collisions," the fraction of V-V energy transfer, f_v , in the self-relaxation of HF was experimentally determined for the first time for all v -levels. For each quenching experiment, the average fractional V-V probability, F_{V-V} , was determined by detailed accounting of the changes of all v -level populations. This F_{V-V} is a weighted average of the desired, specific f_v values. It is clear, therefore, that one wants to start with low vibrational excitation, preferably with $v=1$ and 2 only in which case one would obtain f_2 directly (since $v=1$ has no V-V channel).

In reality, one obtains $v=1,2$, and some 3 from the $\text{F} + \text{H}_2$ and $\text{F} + \text{CH}_4$ generating reactions. The results of ~ 20 quenching experiments provide limits of $0.5 < f_2 < 0.6$ and $0.2 < f_3 < 0.4$. Continuing then to higher v -levels with the $\text{F} + \text{HBr}$ and $\text{H} + \text{F}_2$ generating reactions, one can bracket all f_v values on the assumption that f_v decreases monotonically with increasing v . The results are that $f_2 = 0.55 \pm 0.10$, $f_3 = 0.30 \pm 0.10$, $f_4 = 0.15 \pm 0.10$, and f_5 , f_6 , and f_7 are zero to within their large error bars, i.e. it is quite likely (but not provable) that $f_5 \sim 0.07$, $f_6 \sim 0.03$, and $f_7 \sim 0.01$. These interesting results were compared with theoretical predictions and with one laser double resonance experiment that yielded f_2 0.59 to 0.79 where the lower value was the most likely.

The sixth paper, "Kinetics of Polyatomic Radical Reactions Using a Versatile Flow Reactor Apparatus," describes our new apparatus and provides initial results on the kinetics of the $\text{NH}_2 + \text{NO}$ and $\text{CH}_3\text{O} + \text{NO}_2$ reactions. At the downstream end of the flow tube, three independent detection techniques are used: laser-induced fluorescence (LIF) in the visible or near u.v., vacuum u.v. resonance fluorescence, and modulated molecular

beam mass spectrometry for monitoring "dark" species. Radicals are produced upstream by direct or sensitized infrared laser multiphoton dissociation (MPD) at 10 or 20 Hz and are swept into the flow tube by He carrier gas.

In the first application, NH_2 radicals were produced from N_2H_4 by SF_6 -sensitized MPD and detected by LIF at 597.7 nm synchronized with the dye laser at 200 Hz so that 10 points could be obtained and coherently summed for each NH_2 pulse. NH_2 was then reacted with excess NO, and a rate constant of $0.90 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ was obtained, in very good agreement with other reported results. CH_3 radicals were produced by MPD of $\text{C}_6\text{F}_5\text{OCH}_3$ and reacted with excess NO_2 to produce CH_3O radicals which were monitored by LIF at 298.5 nm. The slower $\text{CH}_3\text{O} + \text{NO}_2$ reaction rate constant was then determined by measuring the pseudo-first-order rate constant of the CH_3O decay as function of excess NO_2 concentration. A detailed study of this reaction is described below. The new, versatile flow reactor apparatus was found to work very well.

In the seventh paper, "Kinetics of the Reaction of CH_3O with NO_2 ," rate coefficients were measured over the temperature range 220–473 K and over the pressure range 0.6–4.0 torr. The reaction has two product channels, CH_3ONO_2 (1a) and $\text{CH}_2\text{O} + \text{HNO}_2$ (1b). The recombination channel, 1a, is likely to be pressure-dependent and to have a negative temperature dependence at lower pressure, near its third-order limit. The H-atom transfer reaction, 1b, is likely to be independent of total pressure and to have a positive temperature dependence. The correctness of these predictions was borne out by the experimental results: At 250 and 298 K, the first-order rate constants were found to be strongly pressure dependent, because the reaction was dominated by the

recombination, 1a, while at 390 K and especially at 473 K, the pressure dependence disappeared, because the reaction was dominated by atom transfer.

All data points were then fitted to an expression that combined a parameterized recombination rate constant, k_{1a} , with a simple Arrhenius expression for k_{1b} . The best fit gave $k_{1a} = 2.6 \times 10^{-29} (T/300)^{-4.5} \text{ cm}^6 \text{ s}^{-1}$ for the low pressure limit of 1a, and $9.6 \times 10^{-12} \exp(-1150/T) \text{ cm}^3 \text{ s}^{-1}$ for the atom transfer, 1b. All of the fitted parameters have large uncertainty limits, but their values seem quite reasonable by comparison with similar reactions.

In the eighth paper, "Kinetics of the Isotope Exchange Reaction of ^{18}O With NO and O_2 at 298 K," the modulated molecular beam mass spectrometer was used to monitor O and NO, their detection limits being in the 10^9 to 10^{10} cm^{-3} concentration range. If the isotope exchange occurs via a relatively long-lived NO_2^+ or O_2^+ intermediate, the measured rate constant is one half of the $\text{O} + \text{NO}$ or $\text{O} + \text{O}_2$ recombination rate constant at its high pressure limit. Earlier published results had given a very low $^{18}\text{O} + \text{NO}$ isotope exchange rate constant, $0.18 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, in poor agreement with the measured high-pressure recombination rate constant, $3.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and with the related vibrational relaxation of $\text{NO}(v=1)$ by O, $k = 6.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Our experiments showed that the isotope exchange process was indeed much faster than had been reported, i.e. $k = (3.7 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, and we were able to show why the low value had been found earlier.

For the $^{18}\text{O} + \text{O}_2$ exchange, earlier measurements had given 0.10 to $0.17 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ whereas we found $(0.29 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ as the result of three different

ways of measuring the isotope exchange rate. The agreement with the measured or calculated high-pressure recombination rate constant is fairly good. Trajectory calculations that used two different potential energy surfaces showed that the exchange process was partly "direct," i.e. did not proceed by way of a long-lived O_3^+ intermediate. This may be due to the relatively weak O-O₂ bond, but needs to be confirmed by further calculations.

3. List of All Publications

1. "Vibrational Relaxation of Highly Excited Diatomics. I. Method, Analysis, and Application to $HCl(v \leq 7) + CO_2$ and N_2O ," B. M. Berquist, J. W. Bozzelli, L. S. Dzelzkalns, L. G. Piper, and F. Kaufman, J. Chem. Phys. 76, 2972 (1982).
2. "Vibrational Relaxation of Highly Excited Diatomics. II. $HCl(v \leq 7) + 20$ Quenchers," B. M. Berquist, L. S. Dzelzkalns, and F. Kaufman, J. Chem. Phys. 76, 2984 (1982).
3. "Vibrational Relaxation of Highly Excited Diatomics. III. $HF(v=5,6,7) + H_2, D_2, N_2, HF, CO_2, N_2O, CH_4$, and C_2H_6 ," L. S. Dzelzkalns and F. Kaufman, J. Chem. Phys. 77, 3508 (1982).
4. "Vibrational Relaxation of Highly Excited Diatomics. IV. $HF(v=1 \text{ to } 7) + HF, CO_2$, and N_2O ," L. S. Dzelzkalns and F. Kaufman, J. Chem. Phys. 79, 3836 (1983).
5. "Vibrational Relaxation of Highly Excited Diatomics. V. The V-V Channel in $HF(v) + HF(0)$ Collisions," L. S. Dzelzkalns and F. Kaufman, J. Chem. Phys. 79, 3363 (1983).
6. "Kinetics of Polyatomic Radical Reactions Using a Versatile Flow Reactor Apparatus," J. B. Jeffries, J. A. McCaulley, and F. Kaufman, Chem. Phys. Lett. 106, 111 (1984).
7. "Kinetics of the Reaction of CH_3O with NO_2 ," J. A. McCaulley, S. M. Anderson, J. B. Jeffries, and F. Kaufman, Chem. Phys. Lett. 115, 180 (1985).
8. "Kinetics of the Isotope Exchange Reaction of ^{18}O With NO and O_2 at 298 K," S. M. Anderson, F. S. Klein, and F. Kaufman, J. Chem. Phys., in press.

4. List of All Participating Scientific Personnel

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